

Description

2.1.3-BENZOTHIADIAZOLES AS ELECTRONIC ACTIVE COMPONENTS

Organic compounds will in the near future be employed as active components (= functional materials) in a variety of different applications which can in the widest sense be considered part of the electronics industry.

In the case of the organic electroluminescence devices based on organic components (for general description of the structure, cf. US-A-4,539,507 and US-A-5,151,629) or their individual components, viz. organic light-emission diodes (OLEDs), introduction onto the market has already occurred, as the car radios with "organic display" obtainable from Pioneer demonstrate. Further such products will be introduced shortly. However, significant improvements are still necessary here in order for these displays to effectively compete with or to surpass the liquid crystal displays (LCDs) which currently dominate the market.

Important conditions for practical use are, in particular, a long operating life, a high stability to heat and a low use and operating voltage in order to make mobile applications possible.

The general structure of organic electroluminescence devices is described, for example, in US 4,539,507 and US 5,151,629.

An organic electroluminescence device usually comprises a plurality of layers which are preferably applied on top of one another by means of vacuum methods. These individual layers are:

1. a support plate = substrate (usually glass or plastic film);
2. a transparent anode (usually indium-tin oxide, ITO);
3. a hole injection layer (= HIL): e.g. one based on copper phthalocyanine (CuPc), conductive polymers such as polyaniline (PANI) or polythiophene derivatives (e.g. PEDOT);
4. a hole transport layer (=HTL): usually one based on triarylamine derivatives;
5. an emission layer (= EML): this layer can coincide partly with layers 4 or 6, but usually comprises fluorescent dyes or host molecules doped with fluorescent dyes;
6. an electron transport layer (= ETL): mostly on the basis of aluminum tris-8-hydroxyquinoxalinate (AlQ₃);
7. an electron injection layer (= EIL): this layer can coincide partly with the layer

6 or a small part of the cathode is specifically treated or specifically deposited;
8. a cathode: here, metals, metal combinations or metal alloys having a low work function are generally used, e.g. Ca, Ba, Mg, Al, In, Mg/Ag.

5 This overall device is, depending on the application, structured, provided with contacts and finally hermetically sealed since the life of such devices is generally reduced drastically in the presence of water and/or air.

10 On application of an appropriate electric potential, holes from the anode and electrons from the cathode are injected into the device and there meet to produce an excited state. This can break down with emission of light. This light is emitted through the transparent anode. In some applications it can also be useful to reverse the arrangement, i.e. to use a (semi)transparent cathode when the anode is, for example, applied to an opaque substrate (for example a silicon chip).

15 In either case, the individual OLED will emit light which has a color determined by the EML. It is in this way possible, depending on the EML, to generate the three basic colors (blue, green, red).

20 A suitable combination of various individual OLEDs then makes it possible to produce a variety of devices ranging from individual light-emitting diodes through simple segmented displays through more complicated matrix displays to full-color, large-format displays/VDUs.

25 The EML functional materials of the abovementioned OLEDs have been or are being intensively optimized. Despite intensive optimization, the characteristic data of the above-described OLEDs have a number of weak points among which two weak points, viz. the short life of the EML materials and the unfavorable efficiency-brightness curves, have proven to be a particular hindrance in the implementation of OLED technology in commercial products:

30 1) The realistic life of the OLED materials available at present under conditions close to practice is severely limited. The life (time after which the luminance has dropped to 50% of the initial luminance) in the red at constant current density and an initial luminance of 100 Cd/cm² is at best a few thousand hours. In the blue, on the other
35 hand, usually only a few hundred to at best from two to three thousand hours are achieved at an initial luminance of 100 Cd/cm².

These lives are insufficient for practical applications and hinder the introduction of OLED devices on the market.

2) It can be seen from the efficiency-brightness curves of conventional materials that the efficiency decreases greatly with increasing brightness. This means that the high brightnesses necessary in practice can be achieved only by means of a high power consumption. However, high power consumptions require high battery powers in portable appliances (mobile phones, laptops, etc.). In addition, the high power consumption, which is mostly converted into heat, can lead to thermal damage to the display.

These deficiencies of the prior art lead to the following objects of the invention: provision of EML materials having a long operating life at industrially feasible luminances in combination with flat efficiency-brightness curves, i.e. materials which display good efficiencies even at high brightnesses.

It has surprisingly been found that particular compounds comprising the 2,1,3-benzothiadiazole unit have excellent properties for use as EML (as pure material or as dopant in a host molecule matrix).

Compounds comprising the 2,1,3-benzothiadiazole unit are subject matter of the present invention. These compounds have the following properties:

1. The emission color of the compounds of the invention can be adjusted over the entire visible region, i.e. from deep blue to deep red, by choice of an appropriate substitution pattern (cf. examples).
2. The 2,1,3-benzothiadiazole-containing compounds of the invention lead, when appropriate devices are used, to excellent operating lives, as example R1 and the operating life measurements carried out therewith show by way of example. Even after 2500 hours of operation, no significant drop in the luminance is observed. This unique behavior resulting from the 2,1,3-benzothiadiazole unit indicates expected lives of >>10 000 hours.
3. The 2,1,3-benzothiadiazole-containing compounds of the invention when used as EML material in electroluminescence devices lead to high efficiencies of the devices, in particular at the industrially desirable high current densities. They make very good efficiencies possible even at high current densities.
4. The 2,1,3-benzothiadiazole-containing compounds of the invention can be prepared with good reproducibility in reliably high purity and display no batch-to-batch fluctuations.
5. The 2,1,3-benzothiadiazole-containing compounds of the invention have a high thermal stability. Choice of suitable substitution patterns enables glass transition temperatures of greater than 100°C to be achieved.

6. The 2,1,3-benzothiadiazole-containing compounds of the invention have excellent solubility in organic solvents. These materials can thus be processed from solution by means of coating or printing techniques. In a preferred embodiment, solutions can be processed together with one or more other compounds which can have either a low molecular weight or a relatively high or high molecular weight. Even in conventional processing by evaporation, this property is advantageous since it makes cleaning of the equipment or the masks used considerably easier.

In addition to the very good properties as EMLs, it has surprisingly been found that particular 2,1,3-benzothiadiazole-containing compounds display excellent properties when used as ETL, as HBL (hole blocking layer) or as host material in the EML, particularly as host material in new types of phosphorescent OLED devices. The use of these compounds in phosphorescent organic electroluminescence devices (for general structure and mode of operation, see: M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Applied Physics Letters, **1999**, 75, 4-6) is therefore likewise subject matter of the present invention.

Looking at the prior art in respect of ETL materials, it is conspicuous that AlQ₃ is used virtually exclusively as ETL in all devices. This compound is also, as mentioned above, frequently used additionally as host material for the EML. Although many attempts have been made to replace this compound by other substances, this has not been successful to date. Up to the present time, AlQ₃ still represents the best compromise for the differing requirements. Thus, the compound has not only a high thermal stability (glass transition temperature $T_g \sim 190^\circ\text{C}$), an obviously usable band position and an acceptable quantum efficiency for fluorescence in the solid state (about 40%). However, a negative aspect is the intrinsic color (absorption: yellow) on the compound which can, particularly in the case of blue OLEDs, lead to color shifts as a result of fluorescence absorption and reemission. This is a particular disadvantage in the abovementioned device structure in which the light is emitted through the cathode, i.e. through the ETL too. Here, blue OLEDs can only be produced with severe deterioration in efficiency or color position. The usability of AlQ₃ in the new types of phosphorescent OLEDs has also not been conclusively clarified.

A further disadvantage of the use of AlQ₃ is the instability toward holes which has now become known from the literature [cf., for example, Z. Popovic et al., Proceedings of SPIE, **1999**, 3797, 310-315] and can always lead to problems in the device in long-term use.

A critical practical disadvantage of AlQ₃ is the strongly hygroscopic nature of this compound. AlQ₃ which is synthesized and stored under normal conditions always contains, in addition to the hydroxyquinoline ligand, one molecule of water per molecule of complex [cf., for example: H. Schmidbaur et al., Z. Naturforsch. **1991**, 46b, 901-911]. This is extremely difficult to remove. For use in OLEDs, AlQ₃ therefore has to be purified in complicated, multistage sublimation processes and subsequently be stored and handled with exclusion of water in a protective gas atmosphere. Furthermore, large fluctuations in the quality of individual AlQ₃ batches and also poor storage stability have been found (S. Karg, E-MRS Conference May 30, 2000-June 2, 2000 Strassbourg).

AlQ₃ is likewise used as ETL in the new types of phosphorescent OLEDs, and in addition the question of the host material for the actual triplet emitters has still not been clarified at all. The use of only a few materials (4,4'-biscarbazolylbiphenyl, polyvinylcarbazole and a triazole derivative) has been reported to date. However, the operating lives are still greatly in need of optimization.

The 2,1,3-benzothiadiazole-containing compounds of the invention which can be used as ETL, as HBL or as host material in the EML are distinguished, especially compared to AlQ₃ and the few host materials known to date for phosphorescent OLEDs, by the following properties:

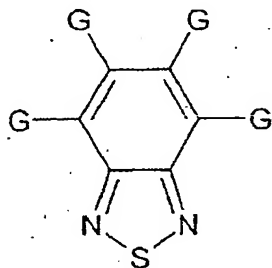
1. They are colorless or virtually colorless; this means that their UV/VIS absorption in the wavelength range from 400 to 700 nm is negligible. In electroluminescence devices according to the invention, this leads to better color purity and high efficiency. This has the advantage that they lead, especially in blue OLEDs, to no color shift or reduction in efficiency. A further advantage is naturally their use as host or ETL material in inverted (cf. above) device geometries.
2. The 2,1,3-benzothiadiazole-containing compounds of the invention when used as host or ETL material in the electroluminescence devices according to the invention lead to high efficiencies which are, in particular, independent of the current densities used. Very good efficiencies are thus made possible even at high current densities.
3. The 2,1,3-benzothiadiazole-containing compounds of the invention have a high oxidation stability. When they are used in appropriate devices according to the invention, this can lead to a significant increase in the operating life. Furthermore, the production of these devices becomes simpler.

4. The 2,1,3-benzothiadiazole-containing compounds of the invention are not noticeably hygroscopic and display a high stability to atmospheric oxygen. Storage for a number of days or weeks in the presence of air and water vapor does not lead to any changes in the substances. Uptake of water by the compounds cannot be detected. This naturally has the advantage that the substances can be purified, transported, stored and prepared for use under simplified conditions. Use does not, in contrast to operations employing AlQ_3 , have to take place entirely under protective gas.

10 In addition, as described above for use as EML materials, they can be prepared reproducibly in good yields and are thermally stable and readily soluble in organic solvents.

15 The use of molecularly defined, uniform, low molecular weight (molar mass < 5000 g/mol) 2,1,3-benzothiadiazole-containing compounds in OLEDs is novel.

The invention provides compounds comprising at least one structural unit of the formula (I),



Formula (I)

20 characterized in that the group G is hydrogen, fluorine and/or an organic radical, the compounds belong to the idealized point group S_n , C_n , C_{nv} , C_{nh} , D_n , D_{nh} or D_{nd} with $n = 2, 3, 4, 5$ or 6 , the molar masses are in the range from 450 g/mol to 5000 g/mol and the melting points are above a temperature of 190°C , with the proviso that they do not contain a macrocycle.

30 The term point group as used here is a term employed in group theory, as described, for example, in: F.A. Cotton, Chemical Applications of Group Theory, 3rd Edition, New York, Wiley, 1990.

For the purposes of the present invention, a macrocycle is a ring having more than eight ring atoms (J.-M. Lehn, Dietrich, Viont, Makrocyclic Compounds Chemistry, Weinheim, VCH Verlag, **1992** and Tetrahedron **1995**, 51, 9241-9284, 9767-9822).

5 The 2,1,3-benzothiadiazole-containing compounds of the invention are highly suitable for use as electroluminescence materials. They can likewise be used as dopants in many host materials.

10 Corresponding OLEDs in which the 2,1,3-benzothiadiazole-containing compounds of the invention are present have both a long life and a high EL efficiency.

15 Prerequisites for this are the above-described symmetry properties. The 2,1,3-benzothiadiazole-containing compounds have to have at least one two-fold or higher rotational axis since in these cases the quantum yield of the fluorescence and thus the quantum yield of the electroluminescence is particularly large and is generally significantly higher than in the case of unsymmetrical compounds of the points C_1 and C_s .

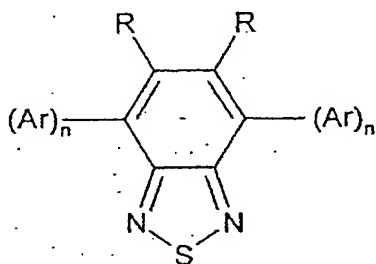
20 A further necessary prerequisite which suitable OLED materials have to fulfill, especially when they are applied by vacuum vapor deposition or vapor deposition in a carrier gas stream, is a molar mass in the range from 450 g/mol to 5000 g/mol. If the molar mass is below the abovementioned range, the vapor pressure is so great that the vacuum equipment will be seriously contaminated even at low temperatures. Secondly, experience has shown that when the upper molar mass limit is exceeded,
25 decomposition-free vaporization is no longer possible.

30 Closely linked to the molar mass are the melting points of the compounds. These have to be above about 190°C, since only then is sufficiently slow and uniform vaporization ensured and only this leads to homogeneous, vitreous films. However, vitreous films are an indispensable prerequisite for functional OLEDs. The melting point of a compound is the temperature at which the phase transition from the solid state to the liquid state takes place.

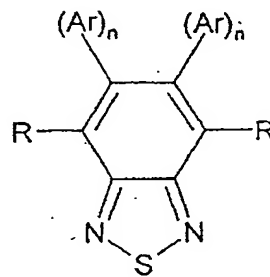
35 In addition, a sufficiently high glass transition temperature in the range above 100°C is a necessary prerequisite for OLEDs which are to be stable over the long term. Experience shows that in suitable organic materials the glass transition temperature is typically at least 60°-90°C below the melting point, so that a melting point of 190°C represents a lower limit for this property, too.

Furthermore, the 2,1,3-benzothiadiazole-containing compounds must not contain any macrocyclic structure, since otherwise they will efficiently complex the palladium used during the synthesis and thus deactivate the coupling catalyst. In addition, these complexes are difficult to separate quantitatively from the product, so that purification of the corresponding compounds is no longer feasible.

The invention likewise provides compounds of the formulae (II) and (III),



Formula (II)



Formula (III)

where the symbols and indices have the following meanings:

the radicals R are identical on each occurrence and are each H, F, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, where one or more nonadjacent CH₂ groups may be replaced by -O-, -S-, -NR¹ or -CONR²- and one or more H atoms may be replaced by F;

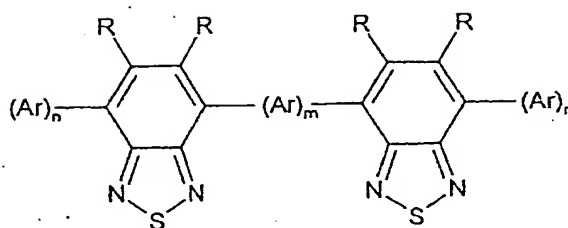
the radicals Ar are identical or different on each occurrence and are each an aryl or heteroaryl group which has from 3 to 30 carbon atoms and may be substituted by one or more nonaromatic radicals R; where a plurality of substituents R, both on the same ring and on the two different rings, may in turn together form a further monocyclic or polycyclic ring system;

R¹, R² are identical or different and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;

n is from 1 to 10, preferably from 1 to 6, particularly preferably 1, 2 or 3.

The property profile of the abovementioned compounds of the formula (II) or (III) in respect of the requirements for OLED applications can be tailored by choice of the substituents Ar. Thus, for example, appropriate choice of the substituent Ar enables the emission color to be set in a targeted manner over the entire visible region from deep red to deep blue (see examples).

The invention likewise provides compounds of the formula (IV),



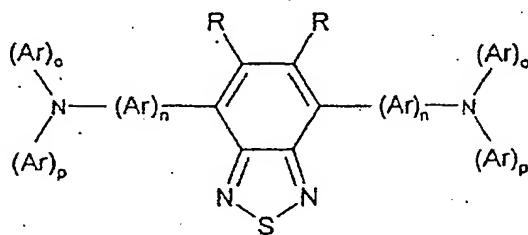
Formula (IV)

where the symbols and indices R, Ar, R^1 , R^2 and n are as defined above and m has the following meaning:

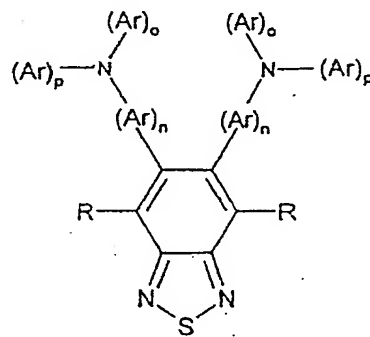
m is from 0 to 4, preferably 1 or 2.

Repetitive concatenation of unconjugated emitting subunits which is achieved, inter alia, by multiple repetition of 2,1,3-benzothiadiazole units and aromatic radicals Ar, viz. compounds of the formula (IV), leads to materials having a correspondingly short emission wavelength (blue emission color) combined with a high molar mass which result in the abovementioned positive properties with regard to vaporization and the glass transition point.

A balanced charge carrier injection (hole or electron injection) into the emission layer and a balanced charge carrier transport in the emission layer are basic prerequisites for efficient OLEDs having a long life. Since the 2,1,3-benzothiadiazole-containing compounds are, as indicated above, good electron conductors, it can in specific cases be found to be advantageous to incorporate hole-conducting units, e.g. triarylamine units as in compounds of the formulae (V) and (VI) in a targeted manner into the emitter material for the EML. Accordingly, compounds of the formula (V) and (VI) are likewise subject matter of the invention:



Formula (V)



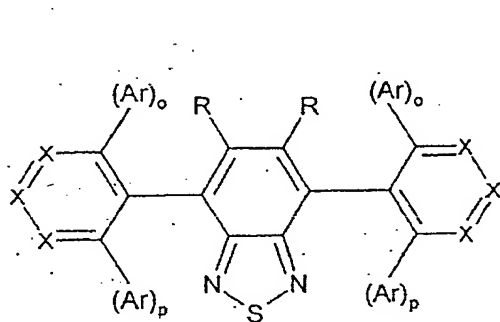
Formula (VI)

where the symbols and indices R, Ar, R^1 , R^2 and n are as defined above and o and p have the following meanings:

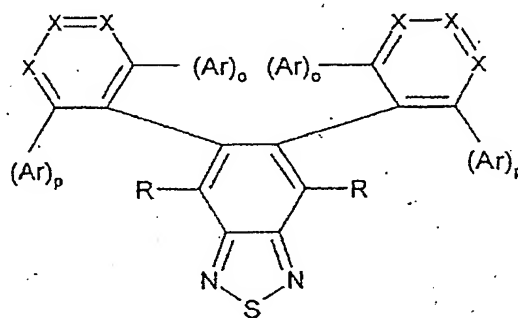
- o is from 1 to 3, preferably 1;
p is from 1 to 3, preferably 1.

Novel 2,1,3-benzothiadiazole-containing compounds of the formulae (V) and (VI) but also (VII), (VIII) and (IX), (X) and (XI) (see below) in which the 2,1,3-benzothiadiazole unit and the joined-on aromatic/ heteroaromatic are strongly twisted relative to one another have a low-lying HOMO (< 5.5 eV relative to the vacuum level) and thus a pronounced stability to oxidation. Accordingly, they are particularly suitable for use as ETL, HBL and also as host material in the EML. In addition, with an appropriate choice of the aromatic/heteroaromatic radicals Ar, they are able to generate triplet states by electron-hole recombination and these can then efficiently be transferred to phosphorescent emitters present as dopants. This property is particularly advantageous in the use of compounds of the formulae (VII) and (VIII) as host material in new types of phosphorescent OLEDs.

The invention also provides compounds of the formulae (VII) and (VIII):



Formula (VII)



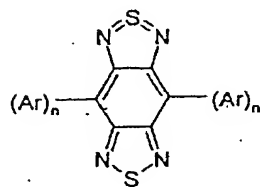
Formula (VIII)

where the symbols and indices R, Ar, R¹ and R² are as defined above and X, o and p have the following meanings:

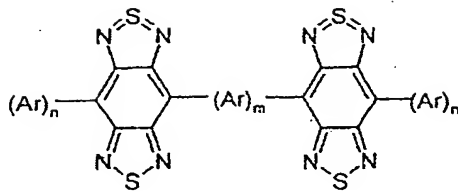
the radicals X are identical or different on each occurrence and are each C(Ar), CR or N;

- o is from 1 to 3, preferably 1;
p is from 1 to 3, preferably 1.

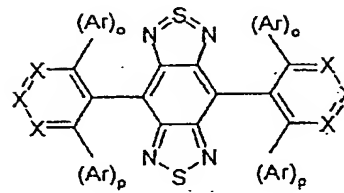
The invention also provides compounds of the formulae (IX), (X) and (XI):



Formula (IX)



Formula (X).



Formula (XI)

where the symbols and indices X, R, Ar, R¹, R², m, n, o and p are as defined above.

Preferred compounds of the formulae (I) to (XI) are characterized in that the aryl or heteroaryl group Ar has from 3 to 24 carbon atoms, particularly preferably from 3 to 14 carbon atoms.

Preferred compounds of the formula (I) to (XI) are characterized in that the radical Ar is benzene, toluene, xylene, fluorobenzene, difluorobenzene, biphenyl, 1,2- or 1,3- or 1,4-terphenyl, tetraphenyl, naphthyl, fluorene, 9,9'-spirobifluorene, phenanthrene, anthracene, 1,3,5-triphenylbenzene, pyrene, perylene, chrysene, triptycene, [2.2]paracyclophane, pyridine, pyridazine, 4,5-benzopyridazine, pyrimidine, pyrazine, 1,3,5-triazine, pyrrole, indole, 1,2,5- or 1,3,4-oxadiazole, 2,2'- or 4,4'-bipyridyl, quinoline, carbazole, 5,10H-dihydrophenazine, 10H-phenoxazine, phenothiazine, xanthene, 9-acridine, furan, benzofuran, thiophene or benzothiophene.

Even though the information given above describes mainly use of the 2,1,3-benzothiadiazole-containing compounds of the invention in OLEDs, it should be pointed out that these compounds can likewise be used very well in the following devices:

1. Use as electron transport material in electrophotography.
2. Use in photovoltaic devices, e.g. organic photodetectors or organic solar cells, as electron acceptor material or electron transport material.
3. Use in organic integrated circuits (O-ICs).
4. Use in organic field effect transistors (OFETs).
5. Use in organic thin film transistors (OTFTs).
6. Use in further applications, some of which have been mentioned above, e.g. organic solid-state lasers.

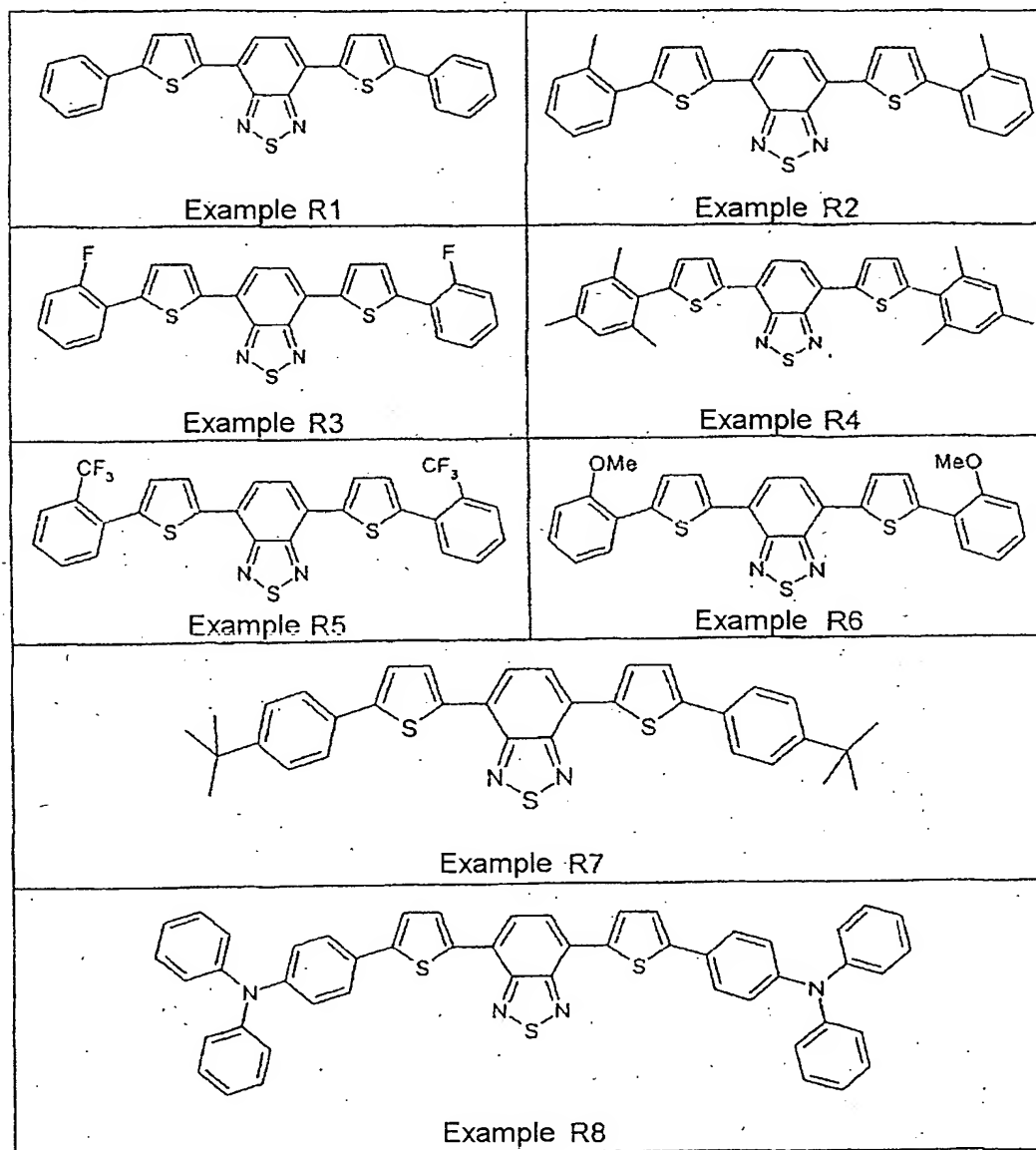
These are likewise subject matter of the present invention.

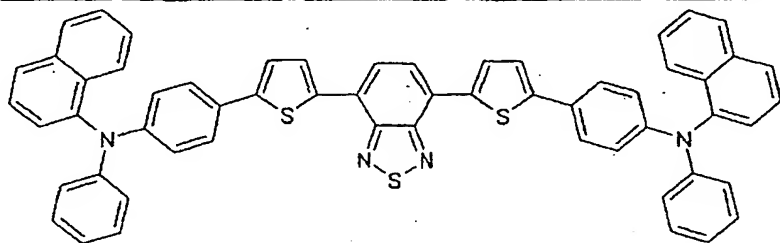
To be able to be used as functional materials, the 2,1,3-benzothiadiazole-containing compounds of the invention are applied in the form of a film to a substrate, generally

by means of known methods with which those skilled in the art are familiar, e.g. vacuum vapor deposition, vapor deposition in a carrier gas stream or from solution by spin coating or using various printing processes (e.g. ink jet printing, offset printing, etc).

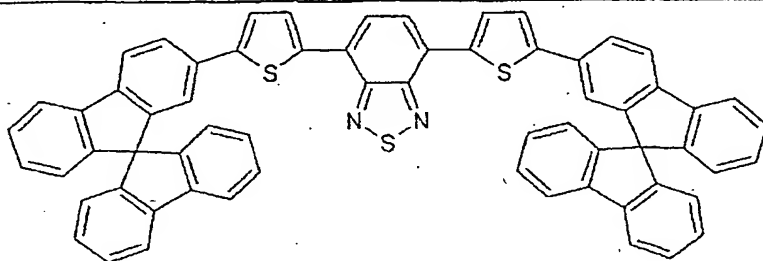
Some examples of the 2,1,3-benzothiadiazole-containing compounds of the invention are given below:

- examples of 2,1,3-benzothiadiazole-containing compounds which have an orange to red emission:

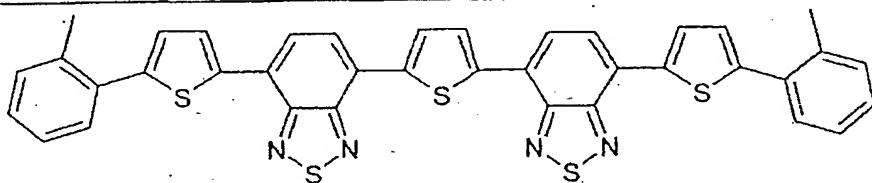




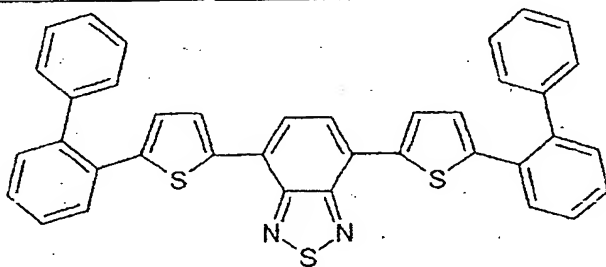
Example R9



Example R10

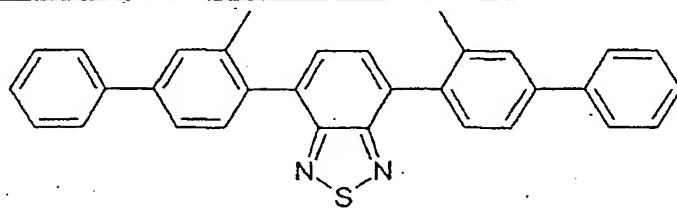


Example R11

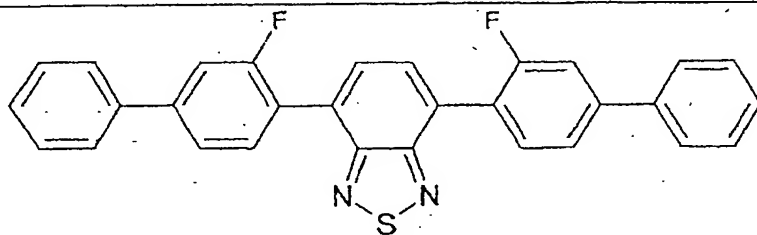


Example R12

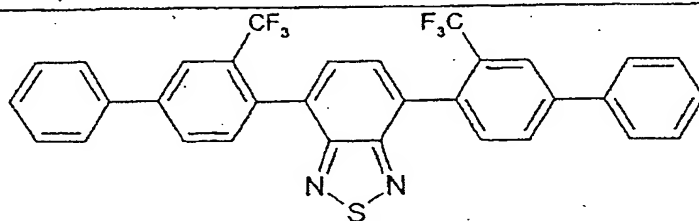
- Examples of 2,1,3-benzothiadiazole-containing compounds which have a green to yellow emission:



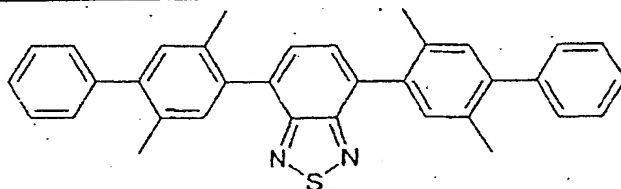
Example G1



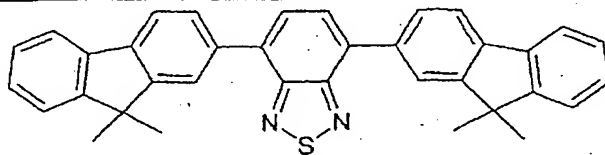
Example G2



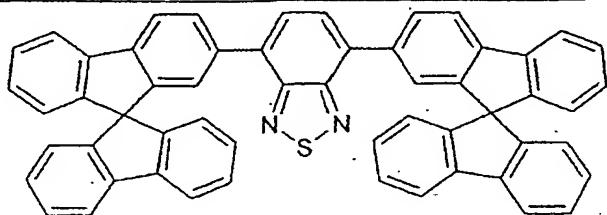
Example G3



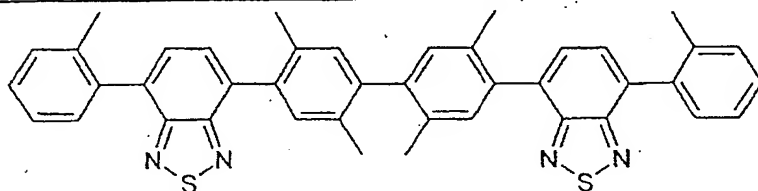
Example G4



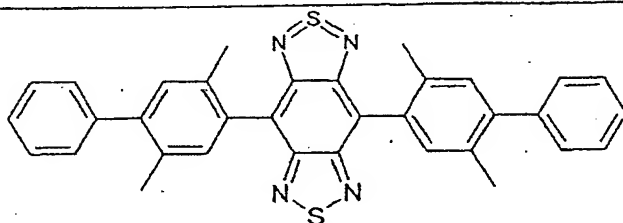
Example G5



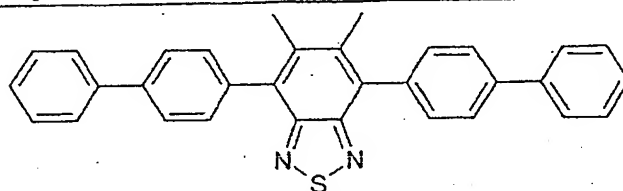
Example G6



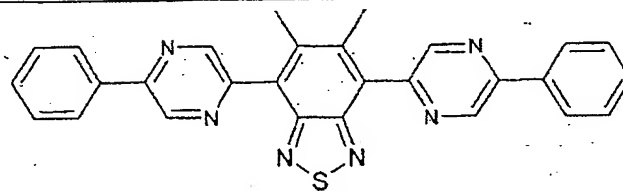
Example G7



Example G8

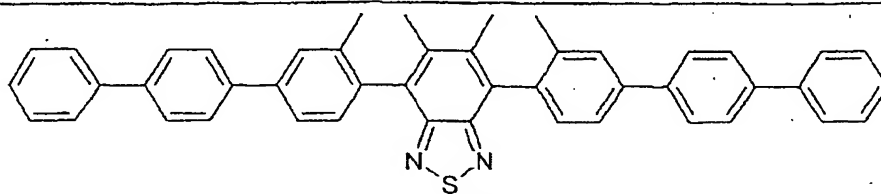


Example G9

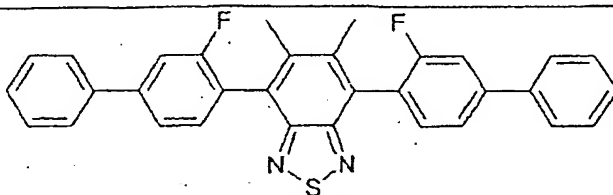


Example G10

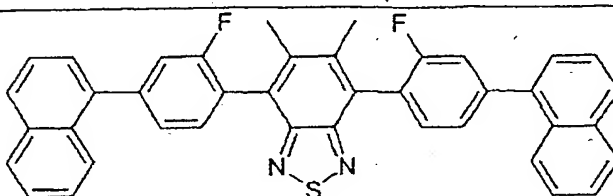
- Examples of 2,1,3-benzothiadiazole-containing compounds which have a dark blue to cyan emission:



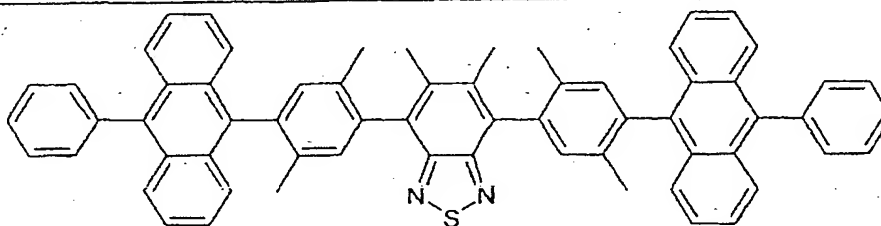
Example B1



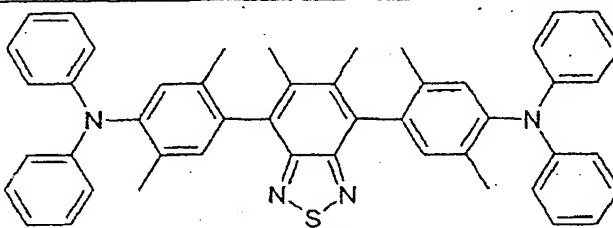
Example B2



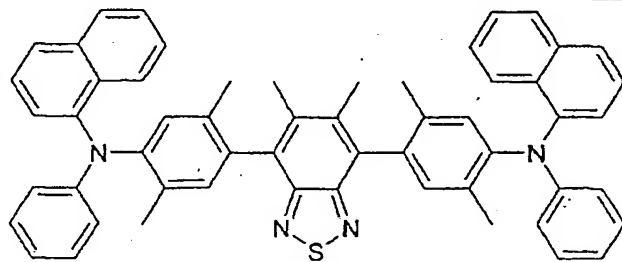
Example B3



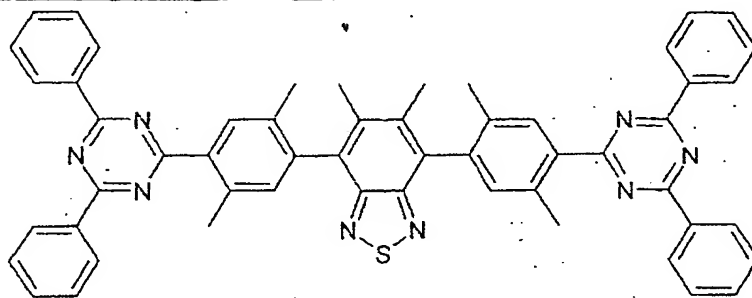
Example B4



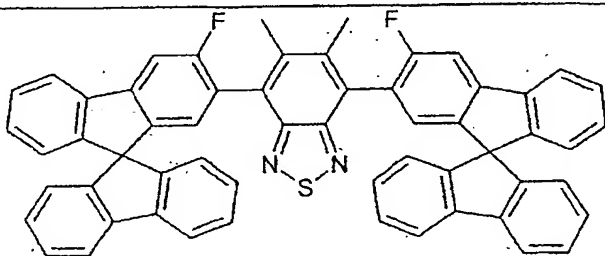
Example B5



Example B6

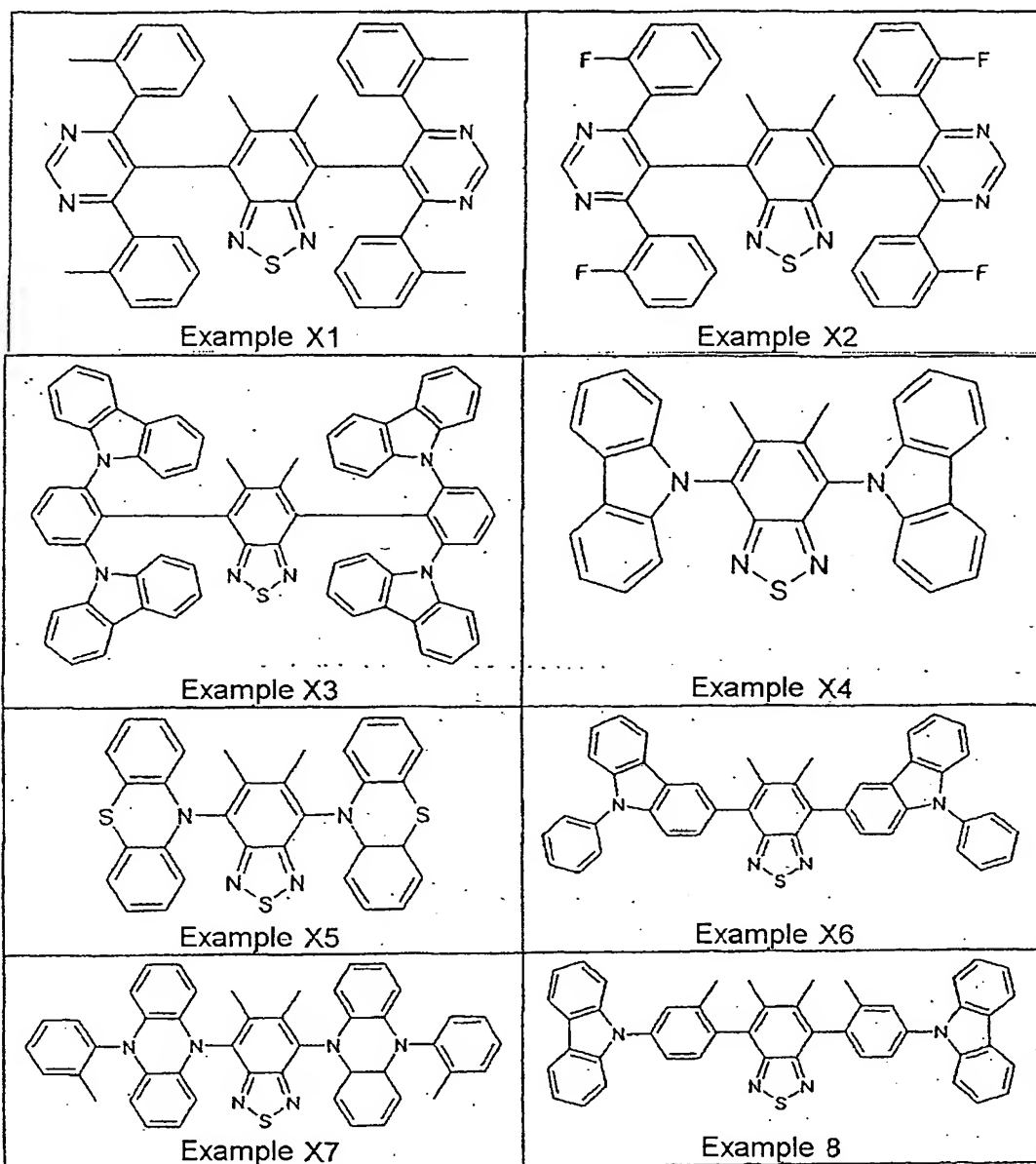


Example B7



Example B8

- Examples of 2,1,3-benzothiadiazole-containing compounds which are used as ETL, HBL and as host material in the EML are:



The 2,1,3-benzothiadiazole-containing compounds were prepared by customary methods with which those skilled in the art are familiar, in particular by means of palladium-catalyzed C-C coupling reactions (e.g. Suzuki coupling) or C-N coupling reactions (Hartwig-Buchwald coupling), from brominated 2,1,3-benzothiadiazoles and arylboronic acids or arylamines.

The present invention is illustrated by the following examples, without being restricted thereto. A person skilled in the art will be able to prepare further

derivatives according to the invention on the basis of the information given without needing to make an inventive step.

1. Synthesis of 2,1,3-benzothiadiazole-containing compounds

The following syntheses were carried out under a protected gas atmosphere unless indicated otherwise. The starting materials were procured from ALDRICH [2,1,3-benzothiadiazole, N-bromosuccinimide, thiopheneboronic acid, phenylboronic acid, o-tolylboronic acid, o-fluoroboronic acid, potassium phosphate, sodium cyanide, tri-*tert*-butylphosphine, palladium(II) acetate, Pd(PPh₃)₄] or from ALFA[4-chloro-2-methylphenylboronic acid] or prepared by literature methods (4,7-dibromo-2,1,3-benzothiadiazole, 4,7-dibromo-5,6-dimethyl-2,1,3-benzothiadiazole: K. Pilgram, M. Zupan, R. Skiles J. Heterocycl. Chem. **1970**, 7, 629).

1.1 Synthesis of relevant precursors

Example P1: Bis-4,7-(2'-thienyl)-2,1,3-benzothiadiazole

13.52 g (11.7 mmol) of Pd(PPh₃)₄ were added to a degassed mixture of 52.92 g (180.0 mmol) of 4,7-dibromo-2,1,3-benzothiadiazole, 60.14 g (470.0 mmol) of thiophene-2-boronic acid, 149.02 g (702.0 mmol) of K₃PO₄, 1000 ml of dioxane and 1000 ml of water. After heating the mixture at 80°C for 7 hours, 4.58 g (93.6 mmol) of NaCN were added. After cooling to room temperature, the aqueous phase was separated. The organic phase was washed twice with H₂O and subsequently dried over Na₂SO₄. After removal of the solvent and recrystallization of the dark red solid twice from dioxane, the product was obtained in the form of red needles. The yield, at a purity of >99.8% (HPLC), was 43.28 g (144.1 mmol) (80.0%).

¹H NMR (CDCl₃, 500 MHz): [ppm] = 8.11 (dd, ³J_{HH} = 3.7 Hz, ⁴J_{HH} = 1.0 Hz, 2H), 7.89 (s, 2H), 7.46 (dd, ³J_{HH} = 5.2 Hz, ⁴J_{HH} = 1.0 Hz, 2H), 7.21 (dd, ³J_{HH} = 5.2 Hz, ³J_{HH} = 3.7 Hz, 2H).

Example P2: Bis-4,7-(5'-bromo-2'-thienyl)-2,1,3-benzothiadiazole

A solution of 7.72 g (25.7 mmol) of bis-4,7-(2'-thienyl)-2,1,3-benzothiadiazole in 770 ml of chloroform was admixed with 9.51 g (54.0 mmol) of N-bromosuccinimide at room temperature with exclusion of light. The mixture was stirred for 6 hours and was subsequently evaporated to a volume of 100 ml, admixed with 300 ml of ethanol, the solid was filtered off with suction and washed three times with 100 ml of ethanol. After drying under reduced pressure (70°C, 1 mbar), the residue was recrystallized three times from DMF. The product was obtained in the form of red crystals. The yield, at a purity of >99.8% (HPLC), was 10.31 g (22.5 mmol) (87.5%).

^1H NMR (DMSO- d_6 , 500 MHz): [ppm]= 8.17 (s, 2H), 7.95 (d, $^3J_{\text{HH}} = 4.2$ Hz, 2H), 7.40 (d, $^3J_{\text{HH}} = 4.2$ Hz, 2H).

Example P3: Bis-4,7-(4-chloro-2-methylphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole

A well-stirred, degassed suspension of 91.13 g (283.0 mmol) of 4,7-dibromo-5,6-dimethyl-2,1,3-benzothiadiazole, 125.41 g (736.0 mmol) of 4-chloro-2-methylbenzeneboronic acid and 300.19 g (2832.0 mmol) of Na_2CO_3 in a mixture of 1800 ml of water and 1800 ml of dioxane was admixed with 809 mg (0.70 mmol) of $\text{Pd}(\text{PPh}_3)_4$ and subsequently refluxed for 16 hours. After cooling, the precipitated solid was filtered off with suction, washed three times with 300 ml of water and three times with 300 ml of ethanol. After drying, the solid was recrystallized twice from 150 ml of toluene and 260 ml of ethanol. The product was obtained in the form of colorless crystals. The yield, at a purity of >99.6% (HPLC), was 98.57 g (238.4 mmol) (84.2%).

^1H NMR (CDCl_3 , 500 MHz): [ppm]= 7.28, 7.27 (2 \times s, 2H), 7.19, 7.18 (2 \times br. s, 2H), 7.06, 7.03 (2 \times br. s, 2H), 2.23 (s, 6H), 1.99, 1.98 (2 \times s, 6H).

1.2 Synthesis of red emitters:

Example R1: Bis-4,7-(5'-phenyl-2'-thienyl)-2,1,3-benzothiadiazole

A degassed mixture of 4.53 g (10.0 mmol) of bis-4,7-(2'-bromo-5'-thienyl)-2,1,3-benzothiadiazole (example P2), 3.66 g (30.0 mmol) of benzenboronic acid, 8.92 g (42.0 mmol) of K_3PO_4 and 1.16 g (1.0 mmol) of $\text{Pd}(\text{PPh}_3)_4$ in 400 ml of dioxane and 400 ml of water was heated at 80°C for 7 hours. After cooling, the mixture was admixed with 0.49 g (10.0 mmol) of NaCN; and after stirring for 15 minutes the aqueous phase was separated off, the organic phase was washed twice with H_2O and subsequently dried over Na_2SO_4 . After removal of the solvent and recrystallization from DMF twice, the product was obtained in the form of red needles. The yield, at a purity of >99.9% (HPLC), was 4.31 g (9.5 mmol) (95.2%).

^1H NMR (DMSO- d_6 , 500 MHz): [ppm]= 8.21 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H), 8.18 (s, 2H), 7.82 (m, 2H), 7.69 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H), 7.47 (m, 4H), 7.37 (m, 4H). Mp.: 229°C

Example R2: Bis-4,7-(5'-(2-methylphenyl)-2'-thienyl)-2,1,3-benzothiadiazole

This was prepared in a manner analogous to example R1. Instead of the benzenboronic acid, 4.08 g (30.0 mmol) of 2-methylphenylboronic acid were used. The yield, at a purity of >99.9% (HPLC), was 4.37 g (9.1 mmol) (91.0%).

^1H NMR (CDCl_3 , 500 MHz): [ppm]= 8.15 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H), 7.91 (s, 2H), 7.52 (m, 2H), 7.29 (m, 6H), 7.19 (d, $^3J_{\text{HH}} = 4.0$ Hz, 2H), 2.53 (s, 6H). Mp.: 198°C

Example R3: Bis-4,7-(5'-(2-fluorophenyl)-2'-thienyl)-2,1,3-benzothiadiazole

This was prepared in a manner analogous to example R1. Instead of the benzeneboronic acid, 4.20 g (30.0 mmol) of 2-fluorophenylboronic acid were used.

The yield, at a purity of >99.9% (HPLC), was 4.28 g (7.2 mmol) (72.0%).

¹H NMR (CDCl₃, 500 MHz): [ppm] = 8.14 (dd, ³J_{HH} = 4.0 Hz, ⁶J_{HF} = 0.67 Hz, 2H), 7.92 (s, 2H), 7.72 (m, 2H), 7.59 (dd, ³J_{HH} = 4.0 Hz, ⁵J_{HF} = 1.34 Hz, 2H), 7.21 (m, 6H).

Mp.: 193°C

Example R12: Bis-4,7-(5'-(2-biphenyl)-2'-thienyl)-2,1,3-benzothiadiazole

This was prepared in a manner analogous to example R1. Instead of the benzeneboronic acid, 5.90 g (30.0 mmol) of 2-biphenylboronic acid were used.

The yield, at a purity of >99.9% (HPLC), was 5.11 g (8.5 mmol) (84.5%).

¹H NMR (CDCl₃, 500 MHz): [ppm] = 8.88 (dd, 2H), 7.68 (s, 2H), 7.66 (m, 2H), 7.40 (m, 6H), 7.32 (m, 10H), 6.68 (d, 2H). Mp.: 191°C.

1.3 Synthesis of green emitters:**Example G6: Bis-4,7-(2-spiro-9,9'-bifluorenyl)-2,1,3-benzothiadiazole**

This was prepared in a manner analogous to example R1. Instead of the benzeneboronic acid, 10.81 g (30.0 mmol) of spiro-9,9'-bifluorene-2-boronic acid were used.

The yield, at a purity of >99.9% (HPLC), was 5.58 g (7.3 mmol) (73.0%).

¹H NMR (CDCl₃, 500 MHz): [ppm] = 7.93 (s, 2H), 7.84 (m, 4H), 7.80 (m, 2H), 7.67 (m, 2H), 7.48 (m, 2H), 7.38 (m, 4H), 7.35 (m, 2H), 7.11 (m, 6H), 6.85 (m, 2H), 6.71 (m, 6H). Mp. >350°C

1.4 Synthesis of blue emitters:**Example B1: Bis-4,7-(2-methylterphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole**

A well-stirred, degassed suspension of 41.34 g (100.0 mmol) of bis-4,7-(4-chloro-2-methylphenyl)-5,6-dimethyl-2,1,3-benzothiadiazole, 55.51 g (280 mmol) of biphenyl-4-boronic acid and 136.84 g (420 mmol) of Cs₂CO₃ in 1500 ml of dioxane was admixed with 243 mg (1.2 mmol) of tri-*tert*-butylphosphene and 225 mg (1.0 mmol) of palladium(II) acetate and subsequently refluxed for 16 hours. After cooling, 1500 ml of water were added and the precipitate formed was washed three times with 300 ml of water and three times with 300 ml of ethanol. After drying, the solid was recrystallized four times from 300 ml of toluene and 100 ml of ethanol. The product was obtained in the form of colorless crystals. The yield, at a purity of >99.9% (HPLC), was 53.14 g (81.9 mmol) (81.9%).

¹H NMR (CDCl₃, 500 MHz): [ppm] = 7.88 (m, 4H), 7.69 (m, 4H), 7.61 (m, 4H), 7.47 (m, 4H), 7.37 (m, 2H), 7.26, 7.25 (2 × s, 2H), 7.14, 7.13 (2 × br. s, 2H), 7.09, 7.08 (2 × br. s, 2H), 2.22 (s, 6H), 1.97, 1.96 (2 × s, 6H). Mp.: 281°C

2. Production and characterization of organic electroluminescence devices comprising the compounds according to the invention

LEDs were produced by the general method outlined below. This naturally had to be adapted in each individual case to the individual circumstances (e.g. layer thickness variation to achieve optimal efficiency or color).

2.1 General method of producing OLEDs

After the ITO-coated substrate (e.g. glass supports, PET film) have been cut to the correct size, they are cleaned in a number of cleaning steps in an ultrasonic bath (e.g. soap solution, Millipore water, isopropanol). To dry the substrates, they are blown with an N₂ gun and stored in a desiccator. Before vapor deposition of the organic layers, the substrates are treated by means of an ozone plasma apparatus for about 20 minutes. It can be advisable to use a polymeric hole injection layer as first organic layer. This is generally a conjugated, conductive polymer, e.g. a polyaniline derivative (PANI) or a polythiophene derivative (e.g. PEDOT, BAYTRON PTM from BAYER). This is then applied by spin coating.

The organic layers are applied in order by vapor deposition in a high-vacuum unit. The layer thickness of the respective layer and the deposition rate are monitored and set by means of a crystal oscillator. It is also possible, as described above, for individual layers to consist of more than one compound, i.e. in general, a host material can be doped with a guest material. This is achieved by covaporization from two or more sources.

Electrodes are then applied to the organic layers. This is generally achieved by thermal vapor deposition (Balzer BA360 or Pfeiffer PL S 500).

The transparent ITO electrode is subsequently connected as anode and the metal electrode (e.g. Ca, Yb, Ba-Al) is connected as cathode and the device parameters are determined.

2.2 Process for producing red OLEDs

Example 1: Red OLED with emitter material from Example R1

Using a procedure analogous to the abovementioned general method, a red-emitting OLED having the following structure was produced:

PEDOT 20 nm (applied by spin coating from water; PEDOT procured from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene])

MTDATA 20 nm (vapor-deposited; MTDATA procured from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine)

5 S-TAD 20 nm (vapor-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene)

AlQ₃ 30 nm (vapor-deposited; AlQ₃ procured from SynTec; tris(quinoxalinato)aluminum(III)) and doped with

10 **R1** 10% by weight (vapor-deposited; bis-4,7-(5'-phenyl-2'-thienyl)-2,1,3-benzothiadiazole prepared as described in example R1)

AlQ₃ 10 nm (vapor-deposited; AlQ₃ procured from SynTec; tris(quinoxalinato)aluminum(III))

Ba 10 nm as cathode

15 Ag 100 nm as cathode protection layer

20 This unoptimized OLED was characterized in a standard fashion; the measured data are shown in figures 1-3. Apart from the flatness of the efficiency curve, which means that high efficiencies can still be achieved even at very high brightnesses (e.g. 10 000 Cd/m²), the excellent operating life of this OLED is a great advantage.

25 **Example 2: Red OLED with emitter material from Example R12**

Using a procedure analogous to the abovementioned general method, a red-emitting OLED having the following structure was produced:

25 PEDOT 20 nm (applied by spin coating from water; PEDOT procured from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene])

MTDATA 20 nm (vapor-deposited; MTDATA procured from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine)

30 S-TAD 20 nm (vapor-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene)

AlQ₃ 30 nm (vapor-deposited; AlQ₃ procured from SynTec; tris(quinoxalinato)aluminum(III)) and doped with

R12 10% by weight (vapor-deposited; bis-4,7-(5'-(2-biphenyl)-2'-thienyl)-2,1,3-benzothiadiazole prepared as described in example R12)

35 AlQ₃ 10 nm (vapor-deposited; AlQ₃ procured from SynTec; tris(quinoxalinato)aluminum(III))

Ba 10 nm as cathode

Ag 100 nm as cathode protection layer

This unoptimized OLED was characterized in a standard fashion; the measured data are shown in figures 4-6. Apart from the flatness of the efficiency curve, which means that high efficiencies can still be achieved even at very high brightnesses (e.g. 10 000 Cd/m²), the excellent operating life of this OLED is a great advantage.

2.3 Method of producing blue OLEDs

Example 3: Blue OLED with emitter material from Example B1

Using a procedure analogous to the abovementioned general method, a blue-emitting OLED having the following structure was produced:

| | |
|------------------|--|
| PEDOT | 20 nm (applied by spin coating from water; PEDOT procured from BAYER AG; poly[3,4-ethylenedioxy-2,5-thiophene]) |
| MTDATA | 20 nm (vapor-deposited; MTDATA procured from SynTec; tris-4,4',4''-(3-methylphenylphenylamino)triphenylamine) |
| S-TAD | 20 nm (vapor-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene) |
| S-DPVBi | 30 nm (vapor-deposited; S-DPVBi prepared as described by H. Spreitzer, H. Schenk, J. Salbeck, F. Weisssoertel, H. Riel, W. Ries, Proceedings of SPIE, 1999 , Vol. 3797; 2,2',7,7'-tetrakis(2,2'-diphenylvinyl)spiro-9,9'-bifluorene) and doped with |
| B1 | 10% by weight (vapor-deposited; 5,6-dimethylbis-4,7-(2,5-dimethylphenyl)-2,1,3-benzothiadiazole prepared as described in example B1), doped into the above S-DPVBi layer |
| AlQ ₃ | 10 nm (vapor-deposited; AlQ ₃ procured from SynTec; tris(quinoxalinato)aluminum(III)) |
| Ba | 10 nm as cathode |
| Ag | 100 nm as cathode protection layer |

This unoptimized OLED was characterized in a standard fashion; the measured data are shown in figures 7 and 8. Apart from the color, a tremendous advantage of this OLED is the flatness of the efficiency curve, which means that high efficiencies can still be achieved even at very high brightnesses (e.g. 10 000 Cd/m²). This is of critical importance especially for use in passive matrix displays.

Abstract

2,1,3-Benzothiadiazoles

The present invention describes novel 2,1,3-benzothiadiazole-containing compounds. Such compounds can be used as active components (= functional materials) in a variety of different applications which can in the widest sense be considered part of the electronics industry.

The compounds of the invention have the formulae (I), (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), (X) and (XI).